AD-A271 747

ATION PAGE

average 1 hour per response, including the time for reviewing instructions, searching existing data sources, ng the collection of information. Send comments regarding this burden estimate or any other aspect of this Washington Headquarters Services, Directorate for Information Operations and Reports 12 5 Jefferson Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.

| | ATE | 3. REPORT TYPE AND DATES COVERED |
| | | 3/1/90 to 2/28/93 *Final* |

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
Photonics and Nonlinear Optics with Molecular Materials and Polymers	61102F 2303/CS

6. AUTHOR(S)

Paras N. Prasad

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
The Research Foundation of State University of New York P. O. Box 9 Albany, NY 12201-0009 AEOSR-TR	93 0806

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
Air Force Office of Scientific Research/NC Directorate of Chemistry and Materials Science Research Bldg. 10 Bolling Air Force Base, DC 20332-6448	F49620-90-C-0021

11. SUPPLEMENTARY NOTES

93-26215

12a. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE, DISTRIBUTION UNLIMITED

SELECTED
NOV 0 2 1993
B

13. ABSTRACT (Maximum 200 words)

We used a multidisciplinary approach to understand the structure-property relationship with an aim towards developing novel second-order and third-order nonlinear materials with enhanced performance for photonics applications. We used a combination of theoretical modeling and experimental measurement of nonlinearities in a group of systematically derivatized structures to understand the structure-property relationship. This approach was extremely useful in designing new structures with enhanced nonlinearities. We have incorporated organic second-order chromophores in sol-gel processed SiO_2 and TiO_2 composites which have been successfully electrically poled to form stable aligned structures. In-situ poling studies while monitoring second harmonic generation and electro-optic modulation were used to study the poling dynamics. The microstructures of sol-gel processed composites were investigated. A combination of optical Kerr-gate, transient absorption and degenerate four-wave mixing was used along with appropriate theoretical development to understand the nature of resonant third-order optical nonlinearity.

14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)

93 10 29 063

FINAL REPORT

PROJECT: Photonics and Nonlinear Optics with Molecular Materials and Polymers

PERIOD: 3/1/90 to 2/28/93

CONTRACT NO: AFOSR F4962090C0021

PRINCIPAL INVESTIGATOR: Dr. Paras N. Prasad, Professor
                                                Photonics Research Laboratory
                                                Department of Chemistry
                                                State University of New York at Buffalo
                                                Buffalo, NY 14214

ABSTRACT

We used a multidisciplinary approach to understand the structure-property relationship with an aim towards developing novel second-order and third-order nonlinear materials with enhanced performance for photonics applications. We used a combination of theoretical modeling and experimental measurement of nonlinearities in a group of systematically derivatized structures to understand the structure-property relationship. This approach was extremely useful in designing new structures with enhanced nonlinearities. We have incorporated organic second-order chromophores in sol-gel processed SiO_2 and TiO_2 composites which have been successfully electrically poled to form stable aligned structures. In-situ poling studies while monitoring second harmonic generation and electro-optic modulation were used to study the poling dynamics. The microstructures of sol-gel processed composites were investigated. A combination of optical Kerr-gate, transient absorption and degenerate four-wave mixing was used along with appropriate theoretical development to understand the nature of resonant third-order optical nonlinearity.

Theoretical (Computational) Studies

For theoretical modeling of optical nonlinearities we have developed unique capabilities where we can utilize three different approaches to compute the nonlinear coefficients: (a) *Ab-initio* time-dependent coupled perturbed Hartree Fock (*ab-initio* TDCPHF), (b) Extended basis set semi-empirical INDO/time-dependent coupled perturbed Hartree-Fock (INDO-TDCPHF) and (c) INDO- sum-over-states method (INDO-SOS). This has permitted us to compare the results of the semi-empirical calculations against the *ab-initio* results as well as against the experimental measurements in order to develop confidence in the predictive ability of the method.

We performed *ab-initio* calculations of static polarizability α and static first and second hyperpolarizabilities β and γ for the haloform series CHX_3, where X = F, Cl, Br, and I using the effective core potential (ECP) approach.[1] The microscopic optical nonlinearities α, β, and γ were calculated as the derivatives of the energy with respect to the electric field, with the energy determined by means of the self-consistent-field approach (SCF), and nonlinearities calculated by means of the coupled perturbed Hartree-Fock (CPHF) formalism. To test the approximation introduced by the ECP method, nonlinear optical responses for the lighter members of the series CHF_3 and $CHCl_3$ were compared with all electron calculations. The effects due to basis set size and inclusion of diffuse and polarization functions of d and f type were examined. The ECP technique was then used to calculate optical nonlinearities for $CHBr_3$ and CHI_3. Although very good agreement was found between calculated and experimental polarizabilities α for the haloform series, the agreement was not as good for the higher order polarizabilities.

For p-nitroaniline the *ab initio* method with a double-zeta basis set which includes semidiffuse polarization functions was used to calculate the dipole moment μ, frequency-dependent linear polarizability α, and nonlinear hyperpolarizabilities β and γ using the time-dependent coupled perturbed Hartree-Fock approach.[2] The computation procedure used here yielded information on the dispersion behavior of all the tensor components of polarizability and various hyperpolarizability terms. The largest dispersion effect was observed for the diagonal components of the polarizability and hyperpolarizability tensors along the long in-plane axis. The magnitudes of the various hyperpolarizability terms which describe the various second-order nonlinear processes showed the following trend: $\beta(-2\omega;\omega,\omega) > \beta(O;\omega,-\omega) = \beta(-\omega;O,\omega) > \beta(O;O,O)$, with $\beta(-2\omega;\omega,\omega)$ exhibiting the largest

frequency dispersion. Similarly for γ the following trend is observed $\gamma(-3\omega;\omega,\omega,\omega) >$ $\gamma(-2\omega;0,\omega,\omega) > \gamma(-\omega;\omega,-\omega,\omega) > \gamma(-\omega;0,0,\omega) \approx \gamma(0;0,\omega,-\omega) > \gamma(0;0,0,0)$ with $\gamma(-3\omega;\omega,\omega,\omega)$ exhibiting the largest frequency dispersion. The results of the literature semiempirical calculations on p-nitroaniline were compared with that of the present *ab initio* calculation, and the problem due to the arbitrary parametrization procedure adopted in the past for semiempirical calculation was discussed. The computed values of the first resonance energy, the dipole moment, and the polarizability were in good agreement with the respective values experimentally observed, within the spread of the existing experimental data. In contrast, the computed β and γ values were considerably smaller than the respective experimentally determined values. We attribute this discrepancy to two sources. First, in the theoretical calculation electron correlation was neglected, and the basis set used, although large, might not still be adequate. Second, there is a considerable spread in the reported experimental values for a given nonlinear coefficient making any comparison between the theory and the experimental difficult.

Frequency-dependent polarizability α and second hyperpolarizability γ corresponding to various third order nonlinear optical processes in benzene were calculated by ab initio time-dependent coupled perturbed Hartree-Fock method.[3] The selection of proper diffuse functions in the basis set was made from a comparison of the calculated values of $\alpha(\omega)$ at two optical wavelengths, (λ = 589 and 632.3 nm) and that of $\gamma(-2\omega;0,\omega,\omega)$ at λ = 1064 nm with the reported experimental values at these wavelengths. It is found that a 4-31G basis with a diffuse p and a diffuse d function, in addition to properly describing various elements, yields the values of α and γ which are, respectively, within 7 and 5% of the corresponding experimental results. The in-plane components of α show a larger frequency dispersion compared to the out-of-plane component. The calculated values of γ for the electric field induced second harmonic generation (EFISH) at five optical wavelengths are within 5 to 14% of the reported experimental results. However, a somewhat larger discrepancy between the calculated and measured values of γ for third harmonic generation (THG) and γ for degenerate four wave mixing (DFWM) is found. The order of the γ values for various third order processes is: $\gamma(THG) > \gamma(EFISH) > \gamma(DFWM) > \gamma(EFIKE) \approx \gamma(EFIOR)$ where EFIKE and EFIOR, respectively represent electric field induced Kerr effect and electric field induced optical rectification. The elements of γ show deviation from the Kleinman symmetry even at lower optical frequencies.

Using a split-valence Gaussian 4-31G basis function augmented with diffuse p and d function and multiconfiguration self-consistent-field optimized geometries, the frequency dependent polarizability α and second hyperpolarizability γ of ethylene, *trans*-butadiene, *trans*-hexatriene, and *trans*-octatetraene molecules have been calculated by the time-dependent coupled perturbed Hartree-Fock *ab initio* method.[4] The calculated values of α and γ are in good agreement with the corresponding gas-phase experimental values at the same fundamental wavelength. The various γ values corresponding to different third-order processes exhibit marked difference in their dependence on the conjugation length. For a specific fundamental frequency, the calculated γ value exhibits the following order:

$\gamma(-3\omega;\omega,\omega,\omega) > \gamma(-2\omega;0,\omega,\omega) > \gamma(-\omega;\omega,\omega,-\omega) > \gamma(-\omega;0,0,\omega) \approx \gamma(0;0,\omega,-\omega)$.

For a comparison of a semi-empirical approach with that of ab-initio the values of polarizability α and second hyperpolarizability γ were computed by the semi-empirical INDO method and by the ab initio method, both utilizing the derivative approach for a group of compounds such as the six carbon atom molecules: hexapentaene, hexadiyne and divinylacetylene.[5] First to examine the dispersion and basis set effects, frequency dependent α and different γ terms, responsible for various third-order nonlinear optical effects, were calculated for hexadiyne by the ab initio time dependent Hartree-Fock method employing both STO-3G and 4-31G basis sets, the latter augmented with p and d semidiffuse functions on carbon. The coupled perturbed Hartree-Fock analytical method was used to compute the various derivatives. Compared to the extended basis results the minimal basis set, STO-3G, is found to heavily underestimate the values of α and γ. The zero frequency limit static α and γ values for hexapentaene, hexadiyne and divinylacetylene were calculated by the ab initio method using both the STO-3G and the augmented 4-31G basis sets. The INDO method was used with the traditionally used minimal basis set involving a single zeta-function to calculate the α and γ values. The required derivatives for this calculation were obtained by the numerical finite field method. For each molecule, the INDO method gives the α and γ values which are significantly lower than those obtained with the extended basis set, augmented 4-31G, but comparable to the results obtained with the minimal basis set, STO-3G, in the ab initio calculation. In the group of six carbon straight chain molecules, α shows an increasing trend with the number of π-electrons but no definite trend is observed for the γ values.

Using the time-dependent coupled perturbed Hartree-Fock approach, frequency-dependent polarizability and hyperpolarizabilities of benzene, aniline, nitrobenzene, and p-nitroaniline were calculated at the intermediate neglect of diatomic differential overlap (INDO) level of molecular orbital theory.[6] To reduce the empirical parameters, the resonance integrals β_{rs} in the INDO approach were calculated explicitly over atomic functions, which also made it possible to extend the basis set. Expressions were derived for calculating β_{rs} and atomic transition moment, μ_{rs} over arbitrary number of atomic functions. Results were obtained using a minimal basis (single zeta) and extended basis (double zeta) in INDO approach and compared with the available *ab initio* and the experimental data. For polarizability and hyperpolarizabilities, the dispersion calculated with the double zeta (DZ) basis set is parallel to the corresponding *ab initio* results, while those obtained with the single zeta (SZ) basis set diverge more rapidly with increasing frequency.

New $\chi^{(2)}$ Materials

Theoretical modeling and chemical synthesis have been used to design a new class of novel thiophene derivative chromophores for second-order nonlinear optics. These molecules, which have a thiophene ring as a donor and a nitro group as an acceptor and various π-conjugation path, show large hyperpolarizability[7] (β). We have found that the thiophene ring acts as a strong donor because of the high lying d orbital of the sulfur atom. Among the molecules investigated, the novel thiophene derivatives show great potentials, with not only large hyperpolarizabilities, but also shorter absorption wavelengths, making them more suitable for frequency doubling applications.

We have made significant progress on developing novel nonlinear molecular materials which do not rely on π-electron conjugation to produce large second-order effects. Crystals of the 1:3 complex between antimony triiodide and sulfur $SbI_3 \cdot 3S_8$ were found to possess a high second order optical nonlinearity.[8] The powder second harmonic generation efficiency was found to be approximately half of that of isostructural complex of iodoform with sulfur $CHI_3 \cdot 3S_8$. Second harmonic generation can be phase matched. The phase matching angle of type I was found to be approximately 30 degrees at the fundamental wavelength 1.064 μm. The Maker fringes measurements gave $\chi_{222}^{(2)} \approx 16$ pm/V, $\chi_{333}^{(2)} \approx 23$ pm/V and $\chi_{311}^{(2)} \approx 15$ pm/V for the values of the components of the second order susceptibility tensor. The third rank hyperpolarizability tensor β was decomposed into irreducible parts,

the norms of the vector part and the septor (octupolar) part in the $SbI_3 \cdot 3S_8$ complex were evaluated to be $\beta_v = 52.1 \times 10^{-40} m^4/V$, $\beta_s = 20.2 \times 10^{-40} m^4/V$.

Langmuir-Blodgett Films of $\chi^{(2)}$ Chromophores

Langmuir-Blodgett films provide a unique opportunity to prepare novel molecular assemblies for nonlinear optics. Stability and good structural correlation in multilayer Langmuir-Blodgett films are important issues. Our work focussed on studying the stability of mixed layers as well as on studying the second harmonic generation and surface plasmon electro-optic modulation in Langmuir-Blodgett films. The surface pressure π of two component monolayers of stearic acid (SA) and 3,4-didecyloxy-2,5-di(4-nitrophenylazomethine) thiophene (DNAT) was measured at the air-water interface by the Wilhelmy method as a function of mean molecular area at various compositions.[9] The surface properties of these mixed films were interpreted in terms of both the additivity rule of molecular areas and the two-dimensional phase rule applied to collapse pressures. Results indicate that SA is miscible with DNAT to up to $\chi_{SA} > 0.5$. At $\chi_{SA} > 0.5$ phase separation occurs and at $\pi > 14$ mN m^{-1} DNAT is ejected from the highly ordered SA film matrix. The index of refraction and thickness of these films dielectrics were determined through surface plasmon (SP) measurements on approximately 500 Å thick silver substrates. Horizontal lifting was used to transfer the Langmuir-Blodgett monolayers to glass slides coated with silver. Mixed solid films of DNAT up to 10% (by weight) in polystyrene matrices with thicknesses ranging from 4 to 12 μm were also prepared, indices and thicknesses being measured using the m-line technique. This allowed us to estimate the index of pure DNAT as a cross-check on the SP results. Since index determinations from these techniques are in essential agreement in terms of linear refractivity, we are able to discuss the structural implications of the SP-measured monolayer film thicknesses.

Second harmonic generation (SHG) and surface plasmon studies were carried out on mono- and multilayer Langmuir-Blodgett (LB) films of an amphiphile containing a small chromophore (N-docosanoyl-4-nitroaniline).[10-12] A quadratic variation in the second harmonic intensity was observed for Y-type multilayers (film thickness above 4 bilayers), but for the thinner films (film thickness less than 4 bilayers) the enhancement of the SHG intensity does not follow the quadratic dependence. The results indicate that the non-linear chromophores lie almost flat on the plane of the substrate with orientation preference in the

dipping direction. The SHG behavior and the second-order nonlinearity of the LB films were compared with those of 2-docosylamino-5-nitropyridine and N-docosyl-4-nitroaniline which also have a chromophore of similar size.

Measurements of electrooptic modulation of surface plasmon resonance were carried out on horizontally transferred Langmuir-Blodgett films of 2-docosylamino-5-nitropyridine.[13] The observed Pockels response is approximately constant for different numbers of layers in multilayered films and is proportional to the strength of the modulating field. The calculated second order susceptibility values are about 2×10^{-13} m/V, two orders of magnitude lower than those derived from second harmonic generation studies. The presence of the Pockels effect was attributed to off-diagonal terms in the second order susceptibility.

Second harmonic generation (SHG) studies were carried out on Langmuir-Blodgett films of 2-docosylamino-5-nitropyridine which were transferred using two different dipping techniques; vertical Y-type and horizontal X-type depositions.[14] The SHG behavior of both types of films can be explained by assuming an average planar symmetry. However, the SHG behavior of horizontally transferred films is remarkably different from that of the vertically transferred films. In Y-type films the SHG is mainly due to the in-plane component $\chi^{(2)}_{yyy}$ (which is along the dipping axis) of the second order nonlinear optical susceptibility tensor and $\chi^{(2)}_{xxx}$ is negligible. In the case of X-type films, also, the SHG is due to the in-plane $\chi^{(2)}$ tensor components but $\chi^{(2)}_{yyy}$ and $\chi^{(2)}_{xxx}$ have comparable magnitudes. In both films the nonlinear optical chromophores lie almost flat with respect to the plane of the substrate. The cancellation of $\chi^{(2)}_{xxx}$ in Y-type films is due to the preferential orientation of molecular domains along the dipping axis. In horizontally transferred films molecular domains seem to be inhomogeneously oriented on the surface.

Sol-Gel Processed Composites [$\cdot \chi^{2)}$]

Sol-gel processing was used to prepare a new class of multicomponent inorganic oxide:organic polymer composites which show great promises for second-order nonlinear optics.[15,16] Special processing technique has permitted the preparation of SiO_2/TiO_2/organic polymer composites in which the relative composition can be judiciously varied to select the linear refractive index for applications in integrated optics. Furthermore, this composite has been doped with both inorganic and organic dopants. The

composite film doped with paranitroaniline (PNA) was successfully poled. Both second-harmonic generation and electrooptic modulation were achieved in such a poled four-component SiO_2/TiO_2/Polymer/PNA composite.

Sol-gel processing technique was also used to prepare a composite with second-order nonlinear optically active molecule, N-(4-nitrophenyl)-(s)-prolinol[17]. Electric-field poling was successfully employed to introduce noncentrosymmetry required for second-order nonlinearity. Studies using *in situ* poling allowed the formulation of conditions under which stable poled orientation was achieved. Second-harmonic generation and electro-optic modulation studies were conducted on this material.

Diethylaminonitrostyrene (DEANST) was doped into different polymer matrices with extremely high concentrations (up to 70% by weight) without loss of optical quality. The polymers used include PMMA and polyvinylcarbazole. The $\chi^{(2)}$ values obtained are over 10^{-7} esu.

We have also successfully prepared composites of DEANST doped with the sol-gel processed silica and TiO_2.[18] The electric field poling procedure was modified in order to achieve the best conditions for the largest obtainable second-order nonlinearity. Temporally and thermally stable $\chi^{(2)}$ values of up to 2×10^{-7} esu have been obtained. An additional means toward enhancing stability of poled structures is the combination of the sol-gel technique with the thermal-induced crosslinking of polymers. This combination of techniques further reduces the rotational freedom for the NLO dopants inside the matrix. It also improved other properties of the material composite, such as mechanical and electrical properties.

Because of the strong solvatochromic effect observed in the chromophore, we are able, using matrices with low dielectric coefficient, to shift the absorption band to shorter wavelength spectral range. This is important for avoiding the reabsorption of the light from second-harmonic generation (wider optical transparency).

Liquid Crystalline Polymers

Second order nonlinear optical susceptibilities of a series of newly synthesized liquid crystalline polymers and corresponding monomers were measured using second harmonic generation.[19] A substituted stilbene moiety was selected as the main conjugated π-electronic structure and systematic modifications were made at the site of the donor and in

the conjugation path in order to compare the role of various donors and charge transferring linkages in the SHG process. The β values extracted from the measurements made on solutions and on thin films yield similar values for the monomers and the corresponding polymers. The variations in β values can be interpreted in terms of molecular structural properties, charge transferring power of the donors and dispersion effect. An electrically aligned chromophore exhibits similar relaxation behavior both in the doped form as a guest in an amorphous polymer matrix and as a side chain of the same amorphous polymer.

Novel Molecular-Ionic Polymers for $\chi^{(2)}$

To take advantage of nonlinearities derived from both molecular and ionic contributions new methacrylate polymers containing the N-alkyl pyridinium salt in the side chain were designed and synthesized.[20] Even though these structures contain counter-ions which can migrate under the influence of applied field, we were successful in poling. The corona poled polymer films showed a large second-order nonlinear optical susceptibility, $\chi^{(2)}$ $(-2\omega;\omega,\omega)$. The larger $\chi^{(2)}$ value of the homopolymer containing N-methylpyridinium salt, compared to that of its copolymer, indicates that the concentration of the nonlinear optical chromophores in the copolymer is lower than the saturation value. The temporal stability of induced alignment of nonlinear optical chromophore seems better than that of many other side-chain polymers and guest-host systems.

In order to enhance the poling efficiency by reducing the prospect of charge migration the small counter-ion (I^- or Br^-) of the salt unit was substituted by a bulky tetraphenylborate (TPB) ion.[21] The corona poled polymer film showed a large second-order nonlinear optical susceptibility, $\chi^{(2)}(-2\omega;\omega,\omega)$. The larger $\chi^{(2)}$ values of these polymers were compared with that of polymer with small counter-ion. It was found that the organoborate unit at the side chain improved the optical quality of the polymeric film compared to the polymer having a small organic counter-ion. Even their monomers could be deposited as a transparent layer on a glass substrate. The temporal stability of the polymer without internal side chain spacer unit was investigated to be better than those of the other polymers with six and ten methylene spacer. Above all, the temporal stability of induced alignment of nonlinear optical chromophore in this TPB series of polymer seems to be better than that of many other side-chain polymers and guest-host systems.

Use of systematically derivatized structures for structure-property relationship

In order to improve our understanding of the molecular structure-nonlinear optical properties relationship, a series of model compounds containing benzothiazole, benzimidazole and benzoxazole units synthesized at Wright Laboratory was studied for their third-order nonlinear optical properties using femtosecond degenerate four-wave mixing.[22] For soluble compounds measurements were made with solutions of various concentrations while for insoluble materials vacuum evaporated films or melt quenched films were used. The time-response behavior as well as concentration dependence of the nonlinearity indicate that there is no one-photon or two-photon resonance encountered at 602 nm, the wavelength of nonlinear optical studies. Therefore, the trend of nonlinearity in the systematically varied model compounds can be related to the structural variations. The present study yields the following information on structure-property relationships: (i) microscopic third-order nonlinearity rapidly increases with an increase of the effective conjugation length for a quasi one dimensional molecule; (ii) incorporation of a sulfur containing heteroaromatic linkage in the conjugated structure enhances the nonlinearity; (iii) transition from a quasi-one dimensional π-electron delocalization to delocalization in two dimensions introduced by using an imidazole N-linkage enhances the third-order optical nonlinearity without reducing the optical transparency window and at the same time improves the solubility. Possible explanations for these structural effects were presented. Also, the observed qualitative trend was compared with that predicted by a recent semi-empirical calculation.

As part of a continuing study, a series of highly conjugated benzobisthiazole, benzobisoxazole, and N,N-diphenylbenzbisimidazole model compounds were synthesized, and their third-order nonlinear optical properties investigated by using subpicosecond degenerate four-wave mixing.[23] Measurements were made at 602 nm on THF solutions, vacuum-deposited films, or melt-quenched films. In all but one material, the third-order effect was determined to be instantaneous within the employed temporal resolution, suggesting dominance of electronic nonlinearity. From the experimental data it was possible to formulate structure-nonlinear optical property correlations and demonstrate that the molecular second hyperpolarizability can be increased almost 3 orders of magnitude by simple structural modifications.

Third-order nonlinear optical properties of several tetrasubstituted cumulenic compounds were studied using subpicosecond degenerate four-wave mixing (DFWM) in the forward geometry.[24] Orientationally averaged third-order hyperpolarizabilities $<\gamma>$ were obtained by comparing the DFWM signal from a solution of the molecules with the signal of a reference liquid (THF). The estimated effective values of $\chi^{(3)}$, the third-order optical susceptibility, of cumulenic compounds with extended conjugation of the π-electron system are high, partly due to the strong nonlinear optical response of the molecules in their ground state, partly due to the resonance enhancement at the operating wavelength, 602 nm.

Third order nonlinear properties of several halomethanes (CH_2Cl_2, $CHCl_3$, CCl_4, CH_2Br_2, $CHBr_3$, CBr_4, CH_3I, CH_2I_2, CHI_3 and CI_4) were measured using the techniques of degenerate four wave mixing (DFWM) at 602 nm and of electric field induced second harmonic generation (EFISH) at the fundamental wavelength of 1064 nm.[25] It was noted that the hyperpolarizabilities determined from DFWM are very close to those measured by EFISH for most halomethanes. The data were interpreted taking into account that third order hyperpolarizabilities measured with DFWM in pure liquids and solutions contain two contributions: electronic and orientational, the latter deriving from ordering of induced dipoles. Estimating the orientational contribution we derived the electronic third order hyperpolarizabilities from DFWM data, and, subsequently, the second order hyperpolarizabilities from EFISH data. A relatively large nonresonance third order susceptibility $\chi^{(3)} = 2.4 \times 10^{-12}$ esu was measured by DFWM in solid iodoform (CHI_3).

Use of composite structures for improvement of bulk optical quality

We reported here the first case (to our knowledge) of a compatible blend between an inorganic polymer, silica glass, and a π-conjugated optical nonlinear polymer, poly (p-phenylene vinylene), homogeneously mixed over large composition ranges.[26] This composite material was prepared by combining sol-gel processing techniques applicable to the silica glass with the preparation of the organic polymer from a water/alcohol soluble sulfonium salt precursor. The organic polymer precursor and the inorganic sol were mixed in a common solvent and converted to the final composite material. The thermal conversion of the organic precursor polymer released HCl which also catalyzed the gelation of the inorganic sol. The composite material was characterized by IR, UV-visible spectral

analysis and thermogravimetric and differential scanning calorimetric analysis. The material can be cast into various forms. Thin films cast by the doctor blading technique exhibit good optical quality and show promise for application in the form of optical wave guides.

The approach used for sol-gel optics i.e. the use of sol-gel processing can play a very important role for the development of novel materials and device structures for nonlinear optics and photonics. Chemical processing using the sol-gel method was used for preparation of new composite materials of both a silica glass and a V_2O_5 gel with a π conjugated polymer poly-p-phenylene vinylene up to 50% by weight.[27-31] The composite films show highly improved optical quality with large third-order nonlinear optical coefficient, the latter derived from the conjugated polymer. Optical waveguiding through the film has been achieved. Nonlinear optical studies using femtosecond degenerate four wave mixing, optical Kerr gate switching and power dependent waveguide coupling have been successfully performed.

A two-dimensional permanent transmission grating was formed on the novel polymer sol-gel composite film by ultrashort (~0.5-ps) and visible (~602-nm) pulsed laser radiation.[32] With an arrangement of three nonco-planar coherent laser beams, we used two approaches to produce direct formation of a two-dimensional grating on the film. One approach is to expose the sample twice to different combinations of two beams, and the other is to expose the sample to three laser beams simultaneously. The diffraction patterns and the relative intensity distributions for different order diffraction of the two-dimensional gratings formed on the poly-p-phenylene vinylene/V_2O_5-gel films are analyzed for the different two-beam combinations and relative orientations among the three laser beams. The total diffraction efficiency for the incident probe laser beam into all the non-zero-order diffraction beams reaches 48%.

It was found that improved optical quality films of poly-p-phenylene benzobisthiazole, often abbreviated as PBZT, and that of a novel composite of PBZT and nylon (Zytel 330) can be produced by extruding hot, critical concentration solutions in methane sulfonic acid.[33] The linear refractive indices and their dispersion behavior in these films were determined by the analyses of the interference fringes observed in the optical transmission spectra. A relatively large value of the linear refractive index is obtained for PBZT. The third-order nonlinear optical susceptibility, $\chi^{(3)}$, is determined for the films of PBZT and PBZT/Zytel composite using subpicosecond degenerate four wave mixing. The $\chi^{(3)}$ value

observed for this PBZT film is almost an order of magnitude larger than that previously reported for PBZT films of a rather inferior quality processed through polyphosphoric acid solution. This result emphasizes the importance of polymer processing to produce better optical quality films for evaluation of intrinsic $\chi^{(3)}$ values of polymers. The response time of the nonlinearity is limited by the laser pulse width, indicating that the nonlinear response is derived from the coherent electronic $\chi^{(3)}$. The $\chi^{(3)}$ value of the PBZT/Zytel composite is lower than that for pure PBZT because of the reduced number density. However, determination of the optical loss, α, in these films yields a much lower value of α for PBZT/Zytel composite film resulting in an improved value of the often used device figure of merit $\chi^{(3)}/\alpha$. This result suggests that composite structures may be useful for optimizing the $\chi^{(3)}/\alpha$ ratio.

Characterization of waveguide and $\chi^{(3)}$ properties of films

We reported on the optical characterization of poly-4-BCMU slab waveguides, and on the fabrication of efficient grating guided-wave couplers using this material.[34,35] Thin film samples were obtained, by spin coating, from a cyclopentanone solution. Grating couplers were used to measure the film refractive indices and thicknesses. Waveguide attenuation was obtained from measurements of the variation in scattering with propagation distance in the visible and near infrared. These parameters allowed us to design, fabricate and test a grating coupler with a coupling efficiency of 45% at 1.064 μm.

Large linear refractive index birefringence, strong dichroic behavior, and highly anisotropic $\chi^{(3)}$ were observed for a uniaxially oriented poly (2,5-dimethoxy paraphenylene vinylene) film.[36] A subpicosecond time-resolved degenerate four-wave mixing study reveals an unusual behavior. Along the draw direction $\chi^{(3)}$ is complex with a negative real part and has a response time that is longer than the optical pulse resolution. In contrast, $\chi^{(3)}$ along the transverse direction is largely real and positive. Its response time is much faster, and is limited by the laser pulse width of ~400 fs.

Studies of Langmuir-Blodgett films of $\chi^{(3)}$ Materials

We also conducted studies of Langmuir-Blodgett films for nonlinear optics.[25,26] Monomolecular films of 3-BCMU, 4-BCMU, and 9-BCMU at the air-water interface were studied[37] by measuring their surface pressure (π) vs surface area per molecule (A)

isotherms as well as by the visible absorption spectra of their polymerized Langmuir-Blodgett (L-B) films. The π-A isotherms of all three n-BCMU monomers displayed a phase transition between an expanded state and a condensed state resembling that of their corresponding polymers. The expanded-state surface areas of 9-BCMU, together with a Corey-Pauling-Koltun (CPK) molecular space-filling model of 9-BCMU, suggest that appreciable diacetylenic-subphase interaction may cause kinking in the looped portions of the side chains. Visible absorption spectra of L-B films of 4-BCMU and 9-BCMU UV polymerized at the air-water interface revealed both a red and a blue form for the former, while the latter was composed of the blue form alone. Horizontally transferring in situ polymerized films of 4-BCMU and 9-BCMU to hydrophobic substrates produced a shift of λ_{max} values to longer wavelengths. Polymerization after transfer to solid substrates resulted in only a blue form polymer for both 4-BCMU and 9-BCMU. The reversibility of the conformation coil to rod transition at the air-water interface was shown to depend on the nature of the side group (i.e., the value of n). Poly-4-BCMU showed 100% conversion back to the coil form after expansion to zero surface pressure, poly-3-BCMU showed only partial conversion, and poly-9-BCMU showed essentially n conversion. In situ polymerized 4-BCMU (blue form and red form) converted completely to the red form after expansion to zero surface pressure, while in situ polymerized 9-BCMU essentially remained in its initial blue form. Polymerization of a six-layer multilayer of 4-BCMU was compared to one having five intervening layers of arachidic acid and revealed a significant decrease in the percent polymerization of the latter. A possible explanation is that polymerization is taking place between adjacent layers as well as within a given layer in multilayers of 4-BCMU.

Resonant $\chi^{(3)}$ processes

With an aim to understand dynamic characteristics of the degenerate four-wave mixing process for molecules with resonant optical hyperpolarizability, we have theoretically and experimentally investigated the compound N,N'-Bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenedicarboximide in chloroform solution using subpicosecond forward degenerate four-wave mixing.[36] It follows from the theoretical and experimental results that a resonant degenerate four wave mixing actually involves two dynamic processes, i.e. a coherent nonlinear response involving four photon parametric mixing and an incoherent nonlinear response due to diffraction from the population grating. The contribution of each process

to the resonant degenerate four wave mixing signal and the dynamic characteristics of each process were discussed. We presented both a theoretical derivation and a numerical simulation for resonant degenerate four wave mixing. An equivalent third-order optical susceptibility $\chi_g^{(3)}$ describing the contribution from the population grating process was introduced. Temporal behavior of the degenerate four wave mixing signal was studied at different incident power intensities and the dependence of signal strength on the intensity was investigated. Numerical simulation using the theoretical model presented here was used satisfactorily to explain the experimental results.

We investigated the influence of two-photon absorption on the third-order nonlinear optical properties of model organic molecules using the technique of degenerate four-wave mixing (DFWM).[39] A theoretical formulation developed here shows that the presence of two-photon absorption, which is related to the imaginary part of the third-order susceptibility $\chi^{(3)}$, leads to an enhancement of the effective third-order nonlinearity and to the appearance of effects caused by the formation of two-photon generated excited states. The dynamic behavior of the nonlinearity is then governed by the properties of excited molecules. The nonlinear effects also involve contributions which depend on the fifth power of the electric field.

We have performed a systematic study of third-order nonlinear optical properties of alkoxy ($-C_{10}H_{21}OCH$) substituted p-polyphenyl oligomers using the technique of time-resolved degenerate four-wave mixing with subpicosecond pulses at 602 nm. Experimentally determined values of the second-order hyperpolarizability $\chi^{(3)}$ for these oligomers increase smoothly from the monomer to the trimer, with a more rapid increase to the pentamer and to the heptamer. In addition, the hyperpolarizabilities for the pentamer and the heptamer appear to be complex. A smooth increase of the γ value is expected from an increase of the π-conjugation from a shorter chain oligomer to a longer chain oligomer. The more rapid increase of the γ value in the pentamer and, especially, in the heptamer, however, can not be satisfactorily explained by only taking into account the π-conjugation length. Two-photon absorption for the pentamer and the heptamer at the measurement wavelength of 602 nm is suggested to be important as the observed dynamic behavior is satisfactorily explained by the predictions of the theoretical model presented here. It is shown that the effective γ value for a two-photon absorbing material is a function of optical intensity, pulse

width, and sample length if one uses the conventional degenerate four-wave mixing description.

Femtosecond response and relaxation of the third order optical nonlinearity in the newly developed poly(p-phenylene vinylene)/sol-gel silica composite were investigated by time-resolved forward wave degenerate four-wave mixing, Kerr gate and transient absorption techniques using 60 femtosecond pulses at 620 nm.[40] Using a theoretical description of two and four-wave mixing in optically nonlinear media it is shown that the results obtained from simultaneous use of these techniques yield valuable information on the real and imaginary components of the third order susceptibility. In the composite material investigated here, the imaginary component is derived from the presence of a two-photon resonance at the wavelength of 620 nm used for the present study. This two-photon resonance is observed as transient absorption of the probe beam induced by the presence of a strong pump beam. It also provides fifth-order nonlinear response both in transient absorption and in degenerate four-wave mixing. The fifth-order contributions are derived from the two-photon generated excited species which can absorb at the measurement wavelength and therefore modify both the absorption coefficient and the refractive index of the medium.

We investigated the dynamics of resonant third order optical nonlinearity of chemically prepared poly(3-dodecylthiophene) by the degenerate four wave mixing technique using 60 femtosecond pulses at 620 nm.[41] The measured effective value of $\chi^{(3)}$ is 5.5×10^{-11} esu, six fold smaller than that obtained with 400 femtosecond pulses, emphasizing the pulse width dependence of effective $\chi^{(3)}$ when the relaxation time of the photo-generated excitation responsible for the optical nonlinearity is comparable to the pulse width. Within the resolution of the optical pulse, the rise time of the nonlinear response is instantaneous and the dominant decay occurs within 200 femtoseconds, revealing that the short time nonlinear response is derived from the initially photo-generated excitons. A detailed analysis of the total decay behavior is consistent with the polaron dynamics of the conformational deformation model proposed by Su, Schrieffer and Heeger for a conjugated linear polymer with bond alternation.

Elastic moduli of a 10:1 uniaxially stretched film of poly-p-phenylene vinylene were determined using the technique of laser-induced acoustic phonon in a degenerate four-wave mixing phase conjugate geometry.[42] The four-wave mixing signal obtained as a function of

film rotation provides acoustic speed as a function of orientation. In order to explain the experimental observation, a theoretical description is presented to describe acoustic wave generated by laser induced transient grating for an arbitrary propagation direction in a medium with any symmetry. This theoretical description also provides the dependence of the acoustic wave on the polarization, propagation direction and the pulse-width of the laser pulses.

The theoretical analysis of our experimental result, using the general Christoffel equation, yielded the complete elastic modulus tensor, both the longitudinal and the shear components. The value of the elastic modulus along draw direction is 46.6 GPa. The analysis also shows a novel feature of mode jump, not reported previously. We observe that within a certain range of angles between the acoustic propagation direction and the draw direction one kind of acoustic mode (quasi-longitudinal) is generated but for another set of angles the mode jumps to become quasi-transverse in nature. The theoretical description presented here also explains this mode-jump behavior.

With the use of a waveguide geometry, CARS spectroscopy was found to be an extremely sensitive technique to detect a very low concentration of molecules dispersed in a matrix.[43] Using a planar optical waveguide geometry, the CARS spectra of 4,4'-dibromobiphenyl dispersed in a $\approx$ 3 μm thick polymethylmethacrylate polymer film cast on a quartz substrate was recorded using picosecond optical pulses. Different vibrational bands were recorded using the TE_O waveguide mode for both the pump and the probe pulses.

We have recently developed a new method which shows that ultrafast optically stimulated birefringence and dichroism may be conveniently investigated by combining polarization sensitive optically heterodyned detection with phase tune-up between the optical Kerr gate signal and the local oscillator.[44] The real and the imaginary parts of complex third-order optical nonlinearity can be effectively separated and their values and signs determined. 60fs pulses at 620 nm were used in experiments carried on tetrahydrofuran solutions of canthaxanthin (4,4'-dioxo-β-carotene). The values of both parts of the complex second hyperpolarizability, γ, as well as the sign of its real part determined by this method compare well with that obtained from the concentration dependence method employing the homodyne-detection optical Kerr gate technique.

Nonlinear response of C_{60}

We undertook correlated theoretical and experimental studies of nonlinear optical properties of the fullerene (C_{60}) molecule.[45] The effort was aimed at understanding the frequency dependence of molecular linear polarizability, α, and molecular second hyperpolarizability, γ, and tied with a simultaneous comparison with a model "two-dimensional" aromatic fullerene analog, the benzene molecule.

In the theoretical part, quantum-mechanical computations were performed using time-dependent coupled-perturbed Hartree-Fock method with an extended basis INDO approach. The α and γ tensors appears to be isotropic, indicating a spherically symmetric, highly delocalized π-electron distribution in C_{60}, and lending further support for the aromatic character of the molecule. The calculations of the effective γ values for various third-order processes (OKG, EFISH, electro-optic Kerr and static hyperpolarizability) were found to have the following order: $\gamma(-\omega;\omega,\omega,-\omega) > \gamma(-2\omega;0,\omega,\omega) > \gamma(-\omega;0,0,\omega) > \gamma(0;0,0,0)$, which is somewhat different than that in benzene where: $\gamma(-2\omega;0,\omega,\omega) > \gamma(-\omega;\omega,\omega,-\omega)$. Experimental investigations of C_{60} were based on complementary techniques of degenerate four-wave mixing with subpicosecond pulses at 602 nm and optical Kerr gate with 60-femtosecond pulses at 620 nm. The derived values of complex second hyperpolarizability are: $\gamma_{re} = -(5\pm2)\times10^{-33}$ esu and $\gamma_{im} = (9\pm1)\times1.^{-33}$ esu. Both wave-mixing techniques indicate ultrafast nonlinear optical response time of fullerene molecule.

Study of photorefractivity in polymers

Our group has recently started both theoretical and experimental studies of photorefractivity in polymeric systems. In this area, we have benefited from our interaction with the group of Dr. Williams at Kodak. For photorefractivity, when a photoconducting polymer is illuminated by light with an intensity that varies sinusoidally with position, the space-charge electric field, hole density, ionized photosensitizer density, and filled hole trap density will also vary with position. Expressions were derived for the zero-order Fourier component of the hole density and the first-order Fourier component of the electric field.[46] The equations take into account the electric field dependence of photocharge generation efficiency and mobility. General equations were simplified for the case in which the trap density is far greater than the density of holes, and for the case in which no hole traps are present. Finally, the zero-order hole density and first-order electric field calculated from

our equations were compared to values obtained by Fourier transforming the results of numerical calculations.

Photorefractive effect was observed in a fullerene (C_{60}) doped organic composite containing poly-vinylcarbazole (PVK) and a second-order molecule, diethyl-amino-nitrostyrene (DEANST).[47] Electrooptic modulation and degenerate four-wave mixing experiments were conducted. The material shows relatively high electrooptic coefficient, photoconductivity quantum efficiency and photorefractive diffraction efficiency.

We also reported an experimental observation of the photorefractive effect in a new polymeric system in which a nonlinear organic polymer was doped with a photosensitizer BDK and a hole transport agent tri-p-tolylamine.[48] The photoconductivity and the electro-optic effect have been studied. The process of the grating formation with the applied field was studied. A strong electric field dependence of the diffraction coefficient has been observed.

Other publications

Other publications reported from our Photonics Research Laboratory are 49-70.

PUBLICATIONS RESULTING FROM CURRENT AFOSR SUPPORT

(Also serves as references for the Progress Report)

1) "Theoretical and Experimental Studies of Optical Nonlinearities of Haloforms CHX_3, X = F, Cl, Br, I", S. P. Karna, M. Dupuis, E. Perrin and P. N. Prasad, J. Chem. Phys. 92, 7418 (1990).

2) "Nonlinear Optical Properties of p-Nitroaniline: An Ab-Initio Time-Dependent Coupled Perturbed Hartree-Fock Study", S. P. Karna, P. N. Prasad and M. Dupuis, J. Chem. Phys. 94, 1171 (1991).

3) "Dispersion of Linear and Nonlinear Optical Properties of Benzene. An Ab-Initio Time-Dependent Coupled-Perturbed Hartree-Fock Study", S. P. Karna, G. B. Talapatra, and P. N. Prasad, J. Chem. Phys. 95, 5873-5881 (1991).

4) "Frequency Dependence of Linear and Nonlinear Optical Properties of Conjugated Polyenes: An Ab Initio Time-Dependent Coupled Hartree-Fock Study", S. P. Karna, G. B. Talapatra, W. M. K. P. Wijekoon, and P. N. Prasad, Phys. Rev. A 45, 2763-2770 (1992).

5) "A Comparative Study of the Nonlinear Optical Properties of Extended π-Electron Structures Obtained by Ab Initio and INDO Methods: Hexapentaene, Hexadiyne and Divinylacetylene", S. P. Karna, Z. Laskowski, G. B. Talapatra and P. N. Prasad, J. Phys. Chem. 95, 6508-6511 (1991).

6) "An Extended Basis INDO Time-Dependent Coupled Perturbed Hartree-Fock Approach to Study Nonlinear Optical Properties of Organic Molecules: Some Benzene Derivatives", G. B. Talapatra, S. P. Karna and P. N. Prasad, submitted for publication to J. Phys. Chem.

7) "Nonlinear Optical Properties of Novel Thiophene Derivatives: Experimental and Ab Initio TDCPHF Studies", S. P. Karna, Y. Zhang, M. Samoc, P. N. Prasad and B. A. Reinhardt, submitted to J. Chem. Phys.

8) "Second Harmonic Generation in Crystalline Complex of Antimony Triiodide-Sulfur", A. Samoc, M. Samoc, P. N. Prasad, and A. Krajewska-Cizio, J. Opt. Soc. Am. 9, 1819 (1992).

9) "Characterization of Langmuir-Blodgett Films of 3,4-didecycloxy-2,5-di(4-nitrophenylazomethine) Thiophene in a Stearic Acid Matrix", L. J. Noe, M. Tomoaia-Cotisel, M. Casstevens, and P. N. Prasad, Thin Solid Films 208, 274 (1992).

10) "Linear and Nonlinear Optical Studies of Mono- and Multilayer Langmuir-Blodgett Films of N-docosanoyl para-nitroaniline", W. M. K. P. Wijekoon, B. Asgharian, P. N. Prasad, T. Giesler and S. Rosenkilde, Thin Solid Films 208, 137 (1992).

11) "Second Harmonic Generation in Langmuir-Blodgett Films of N-docosyl-4-nitroaniline", T. Giesler, S. Rosenkilde, W. M. K. P. Wijekoon, P. N. Prasad and P. S. Ramanujam, in "Frontiers of Polymer Research" Eds. P. N. Prasad and J. K. Nigam, Plenum Press (New York, 1992), p. 157.

12) "Second Harmonic Generation in Anisotropic Langmuir-Blodgett Films of N-docosyl-4-nitroaniline", T. Giesler, S. Rosenkilde, P. S. Ramanujam, W. M. K. P. Wijekoon and P. N. Prasad, Physica Scripta 46, 127 (1992).

13) "Electro-Optic Effect in Langmuir-Blodgett Films of 2-Docosylamino-5-nitropyridine Probed by Surface Plasmon Waves", W. M. K. P. Wijekoon, B. Asgharian, M. Casstevens, M. Samoc, G. B. Talapatra, P. N. Prasad, T. Giesler and S. Rosenkilde, Langmuir 8, 135 (1992).

14) "Second Harmonic Generation Studies of Differences in Molecular Orientation of Langmuir-Blodgett Films Fabricated by Vertical and Horizontal Dipping Techniques", W. M. K. P. Wijekoon, S. P. Karna, G. B. Talapatra and P. N. Prasad, J. Opt. Soc. Am. B. 10, 213 (1993).

15) "Sol-Gel Processed Novel Multicomponent Inorganic Oxide:Organic Polymer Composites for Nonlinear Optics", Y. Zhang, Y. P. Cui, C. J. Wung, P. N. Prasad and R. Burzynski, SPIE Proceedings, Vol. 1560, p. 264 (1991).

16) "A New Class of Sol-Gel Processed Inorganic Oxide:Polymer Composites for Nonlinear Optics and Photonics", Y. Zhang, P. N. Prasad, and R. Burzynski in "Proceedings of Ultra-Structure Conference on Sol-Gel Processing" Orlando, Florida, Ed. L. L. Hench and J. K. West, Wiley, (New York, 1992), p. 825

17) "Second-Order Nonlinear Optical Properties of N-(4-Nitrophenyl)-(S)-Prolinol-Doped Sol-Gel Processed Materials", Y. Zhang, P. N. Prasad and R. Burzynski, Chem. Materials 4, 851 (1992).

18) J. Zieba, Y. Zhang, P. N. Prasad, C. Spenser and R. Burzynski, manuscript under preparation.

19) "Second Order Nonlinear Optical Effects in Novel Liquid Crystalline Polymers and Monomers under Bias of an Applied DC Electric Field", W. M. K. P. Wijekoon, Y. Zhang, S. P. Karna, M. Samoc, P. N. Prasad, A. C. Griffin and A. M. Bhatti, J. Opt. Soc. Am. B 9, 1832 (1992).

20) "Synthesis and Second Order Nonlinear Optical Properties of Polymethacrylates Containing Organic Salt Dye Chromophores", D. H. Choi, H. M. Kim, W. M. K. P. Wijekoon and P. N. Prasad, Chem. Mat. 4, 1253 (1992).

21) "Enhanced Second-Order Nonlinear Optical Effects in New Polymethacrylates Containing Organo-Boron Salt Chromophores", H. M. Kim, D. H. Choi, W. M. K. P. Wijekoon and P. N. Prasad, manuscript under preparation.

22) "Studies of Third Order Optical Nonlinearities of Model Compounds Containing Benzothiazole, Benzoimidazole and Benzoxazole Units", M. T. Zhao, M. Samoc, P. N. Prasad, B. A. Reinhardt, M. R. Unroe, M. Prazak, R. C. Evers, J. J. Kane, C. Jariwala and M. Sinsky, Chem. Materials 2, 670-678 (1990).

23) "Studies of the Third-Order Optical Nonlinearities of Model Compounds Containing Benzobisthiazole, Benzobisoxazole, and Benzobisimidazole Units", B. A. Reinhardt, M. R. Unroe, R. C. Evers, M. T. Zhao, M. Samoc, P. N. Prasad and M. Sinky, Chem. Materials 3, 864-871 (1991).

24) "The Third-Order Nonlinear Optical Properties of Some Tetrasubstituted Cumulenes", I. Kminek, J. Klimovic, and P. N. Prasad, Chem. Materials 5, 357 (1993).

25) "Nonlinear Optical Properties of Halomethanes Studied by Subpicosecond Degenerate Four Wave Mixing and Electric-field Induced Second Harmonic Generation", A. Samoc, M. Samoc, P. N. Prasad, C. Willand and D. J. Williams, J. Phys. Chem. (in Press).

26) "Poly(p-phenylene vinylene) silica Composites: A Novel Sol-gel Processed Nonlinear Optical Material for Optical Waveguide", C. J. Wung, Y. Pang, P. N. Prasad and F. E. Karasz, Polymer 32, 605 (1991).

27) "Sol-Gel Processed Inorganic and Organically Modified Composites for Nonlinear Optics and Photonics" in Advanced Composite Materials, American Ceramic Society publication, Ed. M. Sachs (1991) p. 279.

28) "Sol-Gel Processed Inorganic and Organically Modified Composites for Nonlinear Optics and Photonics", P. N. Prasad, SPIE Proceedings, 1328, 168-173 (1990).

29) "Sol-Gel Processed Inorganic and Organically Modified Composites for Nonlinear Optics and Photonics", P. N. Prasad, "Better Ceramics Through Chemistry IV", Eds. C. J. Brinker, D. E. Clark, D. R. Ulrich and B. J. J. Zelinski, MRS Symposium Proceeding, Vol. 180 (Pittsburgh, 1990), p. 741-746.

30) "Study of Third-Order Optical Nonlinearity and Electrical Conductivity of Sol-Gel Processed Silica: Poly(2-Bromo-5-Methoxy-p-phenylene vinylene) Composite", C. J. Wung, K. S. Lee, P. N. Prasad, J. C. Kim, J. I. Jin, and H. K. Shim, Polymer 33, 4145 (1992).

31) "Third Order Optical Nonlinearity and Conductivity of 2,5-Poly(1,4-Phenylene Vinylene) Composites with Sol-Gel Processed Inorganic Glasses", K. S. Lee, C. J. Wung, P. N. Prasad, C. K. Park, I. C. Kim, Jin and H. K. Shim in "Frontiers of Polymer Research", Eds. P. N. Prasad and J. K. Nigam, Plenum Press (New York, 1992), p. 173.

32) "Two-Dimensional Optical Grating Produced on PPV/V_2O_5-Gel Film by Ultrashort Pulsed Laser Radiation", G. S. He, C. J. Wung, G. C. Xu and P. N. Prasad, Appl. Opt. 30, 3810-3817 (1991).

33) "Third Order Nonlinear Optical Properties of Poly-p-phenylene Benzobisthiazole (PBZT) and its Novel Composite with Zytel Processed Via Methane Sulfonic Acid Solution Extrusion", C. Y-C Lee, J. Swiatkiewicz, P. N. Prasad, R. Mehta and S. J. Bai, Polymer 32, 1195 (1991).

34) "Efficient Grating Coupling and Optical Characterization of Poly-4-BCMU Waveguides" G. Assanto, Q Gong, R. Zanoni, G. I. Stegeman, R. Burzynski and P. N. Prasad, SPIE Proceedings 1216, 254-259 (1990).

35) "Efficient Grating Coupling to Poly-4-BCMU Optical Waveguides", O. Gong, G. Assanto, R. Zanoni, G. I. Stegeman, R. Burzynski and P. N. Prasad, Appl. Opt. 29, 3887-3890 (1990).

36) "Anisotropy of the Linear and Third-Order Nonlinear Optical Properties of a Stretch-Oriented Poly-(2,5-dimethoxy-paraphenylene vinylene)", J. Swiatkiewicz, P. N. Prasad, F. E. Karasz, M. A. Druy and P. Glatkowski, 56, 892-894 (1990).

37) "Interfacial Polymerization of Monomolecular and Langmuir-Blodgett Films of ((Butoxycarbonyl)methyl)Urethane Diacetyienes", J. E. Biegajski, D. A. Cadenhead, and P. N. Prasad, Macromolecules 24, 298-303 (1991).

38) "Dynamic Characteristics of Coherent and Population Grating Processes in Resonant Degenerate Four-Wave Mixing", Y. Cui, M. T. Zhao, G. S. He and P. N. Prasad, J. Phys. Chem. 95, 6842-6848 (1991).

39) "Influence of Two-Photon Absorption on Third-Order Nonlinear Optical Processes as Studied by Degenerate Four-Wave Mixing: The Study of Soluble Didecyloxy Substituted Polyphenyls", M. T. Zhao, Y. Cui, M. Samoc, P. N. Prasad, M. R. Unroe and B. A. Reinhardt, J. Chem. Phys. 3, 864-871 (1991).

40) "Third Order Nonlinearity and Two Photon-Induced Molecular Dynamics: Femtosecond Time Resolved Transient Absorption, Kerr Gate and Degenerate Four-Wave Mixing Studies in Poly(p-phenylene vinylene)/Sol-Gel Silica Film", Y. Pang, M. Samoc and P. N. Prasad, J. Chem. Phys. 94, 5282 (1991).

41) "Photo-Induced Processes and Resonant Third Order Nonlinearity in Poly (3-Dodecylthiophene) Studied by Femtosecond Time Resolved Degenerate Four Wave Mixing", Y. Pang and P. N. Prasad, J. Chem. Phys. 93, 2201-2204 (1990).

42) "Investigation of Laser Induced Acoustic Phonons in Poly(p-phenylene vinylene) Uniaxially Stretched Films", Y. Cui, D. N. Rao and P. N. Prasad, J. Phys. Chem. 96, 5617 (1992).

43) "Wave Guide CARS spectra of 4,4'-Dibromo Biphenyl Dispersed in a PolyMethyl methacrylate Optical Wave Guide", D. N. Rao, R. Burzynski and P. N. Prasad, Opt. Commun. 82, 357 (1991).

44) "Optical Heterodyning of the Phase Tuned Femtosecond Optical Kerr Gate Signal for the Determination of Complex Third-Order Susceptibilities", M. E. Orczyk, M. Samoc, J. Swiatkiewicz, N. Manickam, M. Tomoaia-Cotisel, and P. N. Prasad, Appl. Phys. Lett. 60, 2837 (1992).

45) "Nonlinear Optical Properties of C_{60} Molecule: Theoretical and Experimental Studies", G. B. Talapatra, N. Manickam, M. Samoc, M. E. Orczyk, S. P. Karna, and P. N. Prasad, J. Phys. Chem. 96, 5206 (1992).

46) "Zero-Order and First-Order Theory of the Formation of Space-Charge Gratings in Photoconductive Polymers", J. S. Schildkraut and Y. Cui, J. Appl. Phys. 72, 5055 (1992).

47) "Observation of Photorefractivity in Fullerene Doped Polymer Composites", Y. Zhang, Y. Cui and P. N. Prasad, Phys. Rev. B 46, 9900 (1992).

48) "Photorefractive Effect in a New Organic System of Doped Nonlinear Polymer", Y. Cui, Y. Zhang, P. N. Prasad, J. S. Schildkraut and D. J. Williams, Appl. Phys. Lett. 61, 2132 (1992).

49) "Nonlinear Optical Processes in Polymers and Sol-Gel Glass Composites in Proceedings of "The 4th Ultra Structure Conference", Ed. D. Ulhmann and D. R. Ulrich, John Wiley, (New York, 1992) p. 461.

50) "Nonlinear Optical Effects in Organic Materials", P. N. Prasad in "Nonlinear Optics in Solids" Ed. O. Keller, Springer Ser. Wave Phen. (Springer, Berlin, Heidelberg 1990), 304-327.

51) "Multifunctional Molecular and Polymeric Materials for Nonlinear Optics and Photonics", P. N. Prasad in "Symposium on Multifunctional Materials, Materials Research Society Proceeding, 175, 79-87 (1990).

52) "Is there a Role for Organic Materials Chemistry in Nonlinear Optics and Photonics?" P. N. Prasad and B. A. Reinhardt, Chem. Materials 2, 660-669 (1990).

53) "Third-order Nonlinear Optical Effects in Molecular and Polymeric Materials" P. N. Prasad in "New Materials for Nonlinear Optics", Eds. S. Marder, J. Sohn and G. Stucky, ACS Symposium, Series 455 (Washington, D.C., 1991), p. 50-66.

54) "Strategy for Optimization of Molecular Materials for Nonlinear Optics and Photonics", P. N. Prasad in "Organic Molecules for Nonlinear Optics and Photonics", Eds. J. Messier, F. Kajzar and P. N. Prasad, NATO ASI Series, Vol. 194, Kluwer Academic Publishers (Dordrecht, The Netherlands, 1991), p. 225-237.

55) "Dynamic Polarizability of Haloforms: Experimental and Ab Initio Theoretical Studies", S. P. Karna, E. Perrin, P. N. Prasad and M. Dupuis, J. Phys. Chem. 95, 4329-4332 (1991).

56) "Polymeric Materials for Nonlinear Optics and Photonics", P. N. Prasad, Polymer 32, 1746-1751 (1991).

57) "Photonics and Nonlinear Optics-Materials and Devices" in "Lower-Dimensional Systems and Molecular Devices", Ed. R. M. Metzger, Plenum Press, New York (1991) p. 563-572.

27

58) "Langmuir-Blodgett Films for Nonlinear Optics" in "Lower-Dimensional Systems and Molecular Devices", Ed. R. M. Metzger, Plenum Press, New York (1991) p. 573-577.

59) "Temporal Behavior of Stimulated Kerr Scattering in a CS_2 Liquid-core Hollow Fiber System", G. S. He, G. C. Yu, Y. Pang and P. N. Prasad, J. Opt. Soc. Am. B. 8, 1907-1913 (1991).

60) "Nonlinear Optical Effects in Organic Materials", P. N. Prasad, to be published in "Contemporary Nonlinear Optics" Ed. R. W. Boyd and G. P. Agarwal, Academic Press (San Diego, CA, 1992), p. 265-295.

61) "On the Speed of Optically-Controlled Superconducting Devices", H. S. Kwok, L. Shi, J. P. Zheng, S. Y. Dong, Y. Pang and P. N. Prasad, SPIE Proceedings (in Press).

62) "Polymers for Photonics" in Frontiers of Polymer Research, Eds. P. N. Prasad and J. K. Nigam, Plenum Press, New York (1992) p. 45-62.

63) "Polymers for Photonic Applications", K. S. Lee, M. Samoc, and P. N. Prasad, Comprehensive Polymer Science, Eds. S. L. Agarwal and S. Russo, Pergamon Press (Oxford, 1992) p. 407.

64) "Strategy for Optimization of Molecular and Polymeric Materials For Nonlinear Optics", P. N. Prasad in "Nonlinear Optics - Fundamentals, Materials and Devices", ed. S. Miyata, Elsevier Science Publishers (Amsterdam, 1992) p. 283.

65) "Sol-Gel Processed Inorganic Oxide:Organic Polymer Composites for Second-Order Nonlinear Optics Applications" J. Zieba, Y. Zhang and P. N. Prasad, SPIE Proceedings on Sol-Gel Optics II, Ed. J. D. Mackenzie, 1758, 403-409 (1992).

66) "Characterization of Sol-Gel Processed Poly(p-phenylene vinylene)/silica and V_2O_5 Composites using Waveguide Raman, Raman and FTIR" C. J. Wung, W.M.K.P. Wijekoon, and P. N. Prasad, Polymer 34, 1174-1178 (1993).

67) "Dynamics of Third-Order Nonlinearity of Canthaxanthin Carotenoid by Optically Heterodyned Phase-Tuned Femtosecond Optical Kerr Gate" M. E. Orczyk, M. Samoc, J. Swiatkiewicz and P. N. Prasad, J. Chem. Phys. 98, 2524-2533 (1993).

68) "Characterization of Rhodamine 6G-Doped Thin Sol-Gel Films" U. Narang, F. V. Bright and P. N. Prasad, Appl. Spectroscopy 47, 229-234 (1993).

69) "Multiple Mode-Locking of the Q-Switched Nd-Yag Laser with a Coupled Resonant Cavity" G. S. He, Y. Cui, G. C. Xu and P. N. Prasad, Opt. Commun. 96, 321-329 (1993).

70) "Anisotropy in the Complex Refractive Index and the Third-Order Nonlinear Optical Susceptibility of a Stretch-Oriented Film of Poly(p-phenylene vinylene)" J. Swiatkiewicz, P. N. Prasad and F. E. Karasz, J. Appl. Phys. 74, 525 (1993).

INVITED TALKS AND WORKSHOPS ON RESEARCH SUPPORTED BY AFOSR

1. Materials Research Society, Spring Meeting 1990, San Francisco, CA, April 19, 1990, Symposium on Better Ceramics Through Chemistry IV.
    "Sol-gel Processed Inorganic and Organically Modified Composites For Nonlinear Optics and Photonics".

2. American Chemical Society, Spring Meeting, 1990, Boston, MA, April 22, 1990. Symposium on "New Materials for Nonlinear Optics". A tutorial lecture on
    "Third-order Nonlinear Optical Effects in Molecular and Polymeric Materials".

3. Chemical Research Council, 1st New Industrial Chemistry and Engineering Conference on Future Directions in Polymer Science and Technology, Keystone Resort, CO, May 15, 1990.
    "Nonlinear Optical Properties of Polymers".

4. University of Waterloo, Department of Chemistry Seminar, Waterloo, Ontario, CANADA, May 22, 1990.
    "Nonlinear Optical Effects in Molecular Materials and Polymers".

5. Air Force Nonlinear Optical Polymers Contractors Meeting, Washington, D.C., June 4, 1990.
    "Ultrafast Third-Order Nonlinear Optical Processes".

6. Air Force Nonlinear Optical Polymers Contractors Meeting, Washington, D.C., June 5, 1990.
    "Theoretical Computations of Optical Nonlinearities: Ab Initio vs Semiempirical" S. Karna and P. N. Prasad.

7. "Nonlinear Optics - 1990", Summer School, University of Rochester, NY, June 18, 1990. Tutorial Lecture on
    "Nonlinear Optical Materials".

8. Nippon Oil and Fats, Tsukuba City, Japan, July 2, 1990.
    "Organic Materials for Nonlinear Optics".

9. Japanese Synthetic Rubber Company, Tsukuba City, Japan, July 4, 1990.
    "Nonlinear Optics and Photonics with Organic and Polymeric Materials".

10. Teijin Fundamental Research Laboratory, Tokyo, Japan, July 5, 1990.
    "New Development in Nonlinear Optics of Organic and Polymeric Materials".

11. Mitsui Toatsu Chemicals, Tokyo, Japan, July 6, 1990.
    "New Polymeric and Composite Materials for Nonlinear Optics and Photonics".

12. Tokyo University of Agriculture and Technology, Tokyo, Japan, July 7, 1990.
    "New Developments in Nonlinear Optics of Organic and Polymeric Materials".

13. Showa Denko, Tokyo, Japan, July 9, 1990.
    "Polymeric and Composite Materials for Nonlinear Optics and Photonics".

14. Toshiba R&D Center, Tokyo, Japan, July 10, 1990.
    "Photonics with Molecular and Polymeric Materials".

15. The Symposium of Optics and Electronics, Tokyo, Japan, July 11, 1990.
    "Molecular and Polymeric Materials for Nonlinear Optics and Photonics".

16. SPIE - The International Society for Optical Engineering Meeting, San Diego, CA,
    Symposium on Sol-Gel Optics, July 11, 1990.
    "Sol-Gel Processed Inorganic and Organically Modified Composites for
    Nonlinear Optics and Photonics".

17. SPIE - The International Society for Optical Engineering Meeting, San Diego, CA,
    July 12, 1990. Tutorial Lecture:
    "Introduction to Nonlinear Optical Materials".

18. Specialty Polymers '90, The Johns Hopkins University, Baltimore, MD, August 8, 1990.
    "Third-Order Nonlinear Optical Processes in Molecular and Polymeric
    Materials".

19. NATO Advanced Research Workshop on "Organic Materials for Nonlinear Optics and
    Photonics", LaRochelle, France, August 28, 1990.
    "Strategy for Optimization of Molecular Materials For Nonlinear Optics and
    Photonics".

20. US-UK Optical Glass and Macromolecular Materials Workshop, Keswick, UK, Sept.
    5-7, 1990.
    "Multifunctional Materials for Photonics".

21. 1990 Chemistry Open House, State University of New York at Buffalo, October 13,
    1990.
    "Chemistry and Photonics: A New Frontier of Science and Technology".

22. 43rd Pacific Coast Regional Meeting of the American Ceramic Society, Symposium on Multifunctional Nanocomposites", Seattle, WA, October 27, 1990.
    "Sol-Gel Processed Novel Ceramic-Polymer Composites for Nonlinear Optics and Photonics".

23. Symposium on Composites: Processing, Microstructure, and Properties, Orlando, FL, November 14, 1990.
    "Sol-Gel Processed Inorganic and Organically Modified Composites for Nonlinear Optics and Photonics".

24. First International Conference on Frontiers of Polymer Research, New Delhi, India, January 21, 1991.
    "Polymers for Photonics".

25. 5th International Conference on Ultrastructure Processing, Orlando, FL, February 20, 1991.
    "Photonics and Nonlinear Optics with Polymers and Sol-Gel Processed Glass: Polymer Composites".

26. Johns Hopkins University, Department of Material, Science, Baltimore, MD, March 6, 1991.
    "Photonics and Nonlinear Optics with Polymers and Sol-Gel Processed Glass: Polymer Composites".

27. Polytechnic Institute, Department of Chemistry, Troy, New York, March 21, 1991.
    "Nonlinear Optical Processes in Molecules and Polymers".

28. Pennsylvania State University, Department of Chemistry, April 2, 1991.
    "Polymers and Photonics - A New Frontier of Science and Technology".

29. 150th Annual Chemical Congress of the Royal Society of Chemistry, Symposium on New Electronic Materials, London, U.K., April 11, 1991.
    "Molecular and Polymeric Materials for Nonlinear Optics and Photonics".

30. Hoechst-Celanese, Summit, N.J., April 23, 1991.
    "Nonlinear Optics and Photonics with Novel Molecular Composites".

31. Enichem of America, Princeton, N.J., April 24, 1991.
    "Nonlinear Optics and Photonics with Novel Molecular Composites".

32. Case Western Reserve University, Department of Macromolecular Science, Cleveland, OH, April 26, 1991.
    "Polymers and Photonics - A New Frontier of Science and Technology".

33. CLEO '91, Baltimore, MD, May 14, 1991. Tutorial Lecture on
    "Nonlinear Optics with Organic Materials".

34. University of Washington, Department of Materials Science, Seattle, WA, May 20, 1991.
    "Novel Sol-Gel Processed Inorganic Oxide: Polymer Composite Materials for Photonics".

35. "Nonlinear Optics Summer School, Rochester, NY, June 12, 1991. Tutorial Course
    "Nonlinear Optical Materials".

36. SPIE - The International Society for Optical Engineering Meeting, San Diego, CA, July 23, 1991. Tutorial Lecture on:
    "Introduction to Nonlinear Optical Materials".

37. SPIE - The International Society for Optical Engineering Meeting, San Diego, CA, July 25, 1991 - chaired a session.

38. Korea University, Department of Chemistry, Seoul, KOREA, July 29, 1991.
    "Nonlinear Optical Processes in Conjugated Polymers".

39. Korea Institute of Science and Technology (KIST), Seoul, KOREA, July 29, 1991.
    "Polymeric and Composite Materials for Nonlinear Optics and Photonics".

40. Tongyang Nylon Company, Kyungi-DO, KOREA, July 30, 1991.
    "Polymeric and Composite Materials for Nonlinear Optics and Photonics".

41. Samsung Electronics, Kyung Ki-DO, KOREA, July 30, 1991.
    "Polymeric and Composite Materials for Electronics and Photonics".

42. Korean Research Institute of Chemical Technology (KRICT), Taejon, KOREA, July 31, 1991.
    "Recent Advances in Polymeric and Composite Materials for Nonlinear Optics".

43. Lucky Ltd., R & D Center, Taejon, KOREA, July 31, 1991.
    "Polymeric and Composite Materials for Photonics and Electronics".

44. Pohang Institute of Science and Technology (POSTECH), Department of Materials Science, Pohang, KOREA, August 1, 1991.
    "Nonlinear Optical Effects in Molecules and Polymers".

45. Hoechst Japan, Tokyo, JAPAN, August 9, 1991.
    "Polymeric and Composite Materials for Photonics and Electronics".

46. Tokyo University of Agriculture and Technology, Materials Systems Engineering Department, Tokyo, JAPAN, August 10, 1991.
    "Polymeric and Composite Materials for Nonlinear Optics".

47. US-UK Optical Glass and Macromolecular Materials Workshop, Ilkey, U.K., August 20, 1991.
    "Strategy for Optimization of Molecular and Polymeric Materials for Photonics".

48. Northern Illinois University, Department of Chemistry, DeKalb, Illinois, September 9, 1991.
   "Nonlinear Optical Processes in Molecular and Polymeric Materials".

49. Fifth Toyota Conference on Nonlinear Optical Materials, Nissin, JAPAN, October 9, 1991.
   "Strategy for Optimization of Molecular and Polymeric Materials for Nonlinear Optics".

50. First International Conference on NLO Active Materials, Tokyo, JAPAN, October 11, 1991.
   "Composite Materials for Nonlinear Optics".

51. Nonlinear Optics - Materials, Methods and Components, Stockholm, SWEDEN, October 22, 1991.
   "Nonlinear Optics and Photonics with Molecular, Polymeric and Composite Materials - An Overview".

52. Second ALCOM Symposium, Akron, Ohio, November 6, 1991.
   "Photonics and Nonlinear Optics: An Overview".

53. Materials Research Society Fall Meeting, Symposium on Hierarchically Structured Materials, Boston, Massachusetts, December 4, 1991.
   "Nonlinear Optical Properties of Hierarchical Systems".

54. Air Force Contractors NLO Meeting, Dayton, Ohio, December 9, 1991.
   "Strategy for Optimization of Molecular, Polymeric and Composite Materials for Nonlinear Optics and Photonics".

55. US-India Workshop on Frontiers of Research in Polymers and Advanced Materials, Goa, INDIA, January 8, 1992.
   "Molecular Materials and Structure-Property Relationship for Photonics".

56. SPIE - The International Society for Optical Engineering Meeting, Los Angeles, CA, January 22, 1992 – chaired a session on Nonlinear Optics.

57. University of Alabama, Department of Chemistry, Tuscaloosa, Alabama, February 21, 1992.
   "Nonlinear Optical Effects in Molecules and Polymers".

58. Lubrizol Corporation, Ohio, February 26, 1992.
    "Electroactive Polymers – Issues, Opportunities and Role of Computational Chemistry".

59. Case Western Reserve University, Department of Chemistry, February 27, 1992.
    "Nonlinear Optical Effects in Molecules and Polymers".

60. State University of New York at Stony Brook, Department of Chemistry, March 20, 1992.
    "Chemistry and Photonics – A New Frontier of Science and Technology".

61. CLEO '92, Annheim, CA, May 12, 1992, Tutorial Lecture on:
    "Nonlinear Optics with Organic Materials".

62. Computational Chemistry and Nonlinear Optics Workshop, Dayton, Ohio, May 20, 1992.
    "Computational Chemistry and Nonlinear Optics: Issues and Opportunities".

63. 34th IUPAC International Symposium on Macromolecules, Prague, Czechoslovakia, July 14, 1992.
    "Nonlinear Optical Processes in Polymers".

64. Nonlinear Optics Summer School, Rochester, NY, July 17, 1992. Tutorial Course:
    "Nonlinear Optical Materials".

65. SPIE – The International Society for Optical Engineers Meeting, San Diego, CA. Symposium on Sol-Gel Optics II, July 21, 1992.
    "Novel Sol-Gel Processed Multicomponent Inorganic Oxide:Organic Composite Materials for Nonlinear Optics and Photonics".

66. Gordon Research Conference on Electronic Processes in Organic Solids, Andover, NH, July 30, 1992.
    "Nonlinear Optical Effects in Molecular, Polymeric, and Composite Materials".

67. 3rd International Symposium on Organic Materials for Nonlinear Optics, OMNO 92, Oxford, U.K., August 21, 1992
    "Recent Advances in Polymeric and Composite Materials for Nonlinear Optics".

68. PPG Industries, Inc., Chemicals Group Technical Center, Monroeville, PA, October 12, 1992.
    "Non-linear Optics with Molecular Materials".

69. Second International Conference on Frontiers of Polymers and Advanced Materials, Jakarta, INDONESIA, January 12, 1993.
    "Novel Polymeric Composite Materials for Photonics".